

# Spectral and photochemical behaviour of mononuclear and dinuclear $\alpha$ -diimine complexes of Pt(II) and Pd(II) with catechol derivatives

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Received 21 February 1994; accepted 15 November 1994

## Abstract

Mononuclear and dinuclear complexes with the formulae  $[M(\text{DHB})(\text{N-N})]$  (where  $M \equiv \text{Pd(II)}$  or  $\text{Pt(II)}$ ;  $\text{N-N} \equiv 2,2'$ -bipyridine (BPY), 2,2'-biquinoline (BIQ), 4,7-diphenyl-1,10-phenanthroline (DPP) or 1,10-phenanthroline (PHEN); DHB is the dianion of 3,4-dihydroxybenzaldehyde) and  $\{[M(\text{BPY})_2(\text{THB})]\}$  (where  $M \equiv \text{Pd(II)}$  or  $\text{Pt(II)}$ ; BPY is 2,2'-bipyridine; THB is the tetraanion of 3,3,4,4-tetrahydroxybenzaldazine) photosensitize the oxidation of 2,2,6,6-tetramethyl-4-piperidinol (XH) in *N,N*-dimethylformamide (DMF) to give 4-hydroxy-2,2,6,6-tetramethyl-4-piperidinyloxy, a nitroxide free radical (XO). This photo-oxidation reaction involves singlet molecular oxygen ( $^1\text{O}_2$ ) as an intermediate and its presence is confirmed by quenching studies using bis(diethylthiocarbamate)nickel(II) ( $\text{Ni}(\text{DDTC})_2$ ), a physical quencher of  $^1\text{O}_2$ . The ability of the mononuclear complexes to photosensitize the above photo-oxidation reaction follows the order:  $[\text{Pt}(\text{DHB})(\text{PHEN})] > [\text{Pt}(\text{DHB})(\text{DPP})] > [\text{Pt}(\text{DHB})(\text{BIQ})] > [\text{Pt}(\text{DHB})(\text{BPY})] > [\text{Pd}(\text{DHB})(\text{DPP})] \geq [\text{Pd}(\text{DHB})(\text{PHEN})] > [\text{Pd}(\text{DHB})(\text{BIQ})] \geq [\text{Pd}(\text{DHB})(\text{BPY})]$ . Moreover, the dinuclear complexes, in comparison with the analogous mononuclear complexes, follow the order:  $\{[\text{Pt}(\text{BPY})_2(\text{THB})]\} > [\text{Pt}(\text{DHB})(\text{BPY})] > \{[\text{Pd}(\text{BPY})_2(\text{DHB})]\} > [\text{Pd}(\text{DHB})(\text{BPY})]$ . These orders depend on the metal ion, the number of metal ions in the complex, the nature of the  $\alpha$ -diimine ligand and the distortion from planar geometry of the metal complex.

**Keywords:** Mononuclear  $\alpha$ -diimine complexes; Dinuclear  $\alpha$ -diimine complexes; Catechol derivatives

## 1. Introduction

The involvement of  $^1\text{O}_2$  in a number of chemical and biological processes is well established [1–3]. Several examples of luminescent metal complexes, involving electron transfer [4,5] and energy transfer [6,7] processes, have been reported. Mixed-ligand complexes containing reducing and oxidizing ligands show a typical optical electronic transition called a ligand-to-ligand charge transfer (LLCT) transition [8–10]. Several mixed-ligand complexes undergo photo-oxidation on irradiation at the LLCT band [11,12]. Many  $d^8$  metal complexes with catecholate and  $\alpha$ -diimine ligands generate  $^1\text{O}_2$  on irradiation at the LLCT band [13].

Recently, there has been considerable interest in the photochemical and photophysical properties of binuclear and multinuclear transition metal complexes containing bridging ligands which allow varying degrees of electronic interaction between the coupled metal centres

[14]. Complexes of this type are of interest as potential chromophores for multiple binding sites and multi-electron photoredox processes. Binuclear complexes of  $d$  metal ions have been found to have relatively long-lived excited states. Such long-lived excited states can participate in intermolecular electron transfer or energy transfer reactions, which often play a key role in multistep schemes for the conversion of light into chemical energy [15].

A study of the effect of the  $\pi$ -acceptor ability of the  $\alpha$ -diimines in the complexes on the LLCT band and the photoproduction of  $^1\text{O}_2$  is of interest. Hence several Pt(II) and Pd(II) complexes with the formula  $[M(\text{DHB})(\text{N-N})]$  were studied (where  $\text{N-N}$  represents the various  $\alpha$ -diimines, such as 4,7-diphenyl-1,10-phenanthroline (DPP), 2,2'-bipyridine (BPY), 2,2'-biquinoline (BIQ) and 1,10-phenanthroline (PHEN);  $M \equiv \text{Pt(II)}$  or  $\text{Pd(II)}$ ; DHB is the dianion of 3,4-dihydroxybenzaldehyde ( $\text{H}_2\text{DHB}$ )). In order to investigate the electronic advantage of binuclear complexes over mononuclear complexes, complexes with the formula

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$\{[M(\text{BPY})]_2(\text{THB})\}$  (where  $M \equiv \text{Pd}(\text{II})$  or  $\text{Pt}(\text{II})$ ;  $\text{BPY} \equiv 2,2'$ -bipyridine;  $\text{THB}$  is the tetraanion of 3,3,4,4-tetrahydroxybenzaldazine) were also studied.

## 2. Experimental details

### 2.1. Materials

The preparation and characterization of the complexes  $[\text{Pd}(\text{DHB})(\text{BPY})]$  (1),  $[\text{Pd}(\text{DHB})(\text{PHEN})]$  (2),  $[\text{Pd}(\text{DHB})(\text{BIQ})]$  (3),  $[\text{Pd}(\text{DHB})(\text{DPP})]$  (4),  $[\text{Pt}(\text{DHB})(\text{BPY})]$  (5),  $[\text{Pt}(\text{DHB})(\text{PHEN})]$  (6),  $[\text{Pt}(\text{DHB})(\text{BIQ})]$  (7),  $[\text{Pt}(\text{DHB})(\text{DPP})]$  (8),  $\{[\text{Pd}(\text{BPY})]_2(\text{THB})\}$  (9) and  $\{[\text{Pt}(\text{BPY})]_2(\text{THB})\}$  (10) have been reported elsewhere [16]. Bis(diethyldithiocarbamate)nickel(II) ( $\text{Ni}(\text{DDTC})_2$ ) was prepared as described in Ref. [17]. Rose bengal and 2,2,6,6-tetramethyl-4-piperidinol (XH) (Aldrich, USA) were of reagent grade and were used as received. Other reagents and solvents were purified before use by standard procedures [18].

### 2.2. Physical measurements

The physical methods used have been reported elsewhere [19,20].

### 2.3. General irradiation procedure

- (1) Irradiation was carried out on a merry-go-round apparatus. The stabilized light source of a 250 W tungsten-halogen lamp operating at 20 V was housed at the centre of a double-jacketed Pyrex vessel thermostatically controlled at  $28 \pm 1$  °C by water circulating through the outer jacket; a filter solution (7%  $\text{NaNO}_2$ ) was used in the inner jacket to cut off light wavelengths below 400 nm [21]. The solutions to be irradiated were placed in Pyrex tubes (20 cm  $\times$  1 cm) and bubbled with molecular oxygen for 10 min before irradiation. The solutions were placed on the merry-go-round apparatus about 5 cm away from the light source and were revolved at a speed of 33 rev  $\text{min}^{-1}$ .
- (2) Typically, molecular-oxygen-saturated *N,N*-dimethylformamide (DMF) solutions of  $[\text{M}(\text{DHB})(\text{N-N})]$  ( $2 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) and  $\{[\text{M}(\text{BPY})]_2(\text{THB})\}$  ( $1 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) were irradiated in the presence of XH ( $2 \times 10^{-2}$  mol  $\text{dm}^{-3}$ ) at wavelengths of 400–800 nm for different time intervals. The  $^1\text{O}_2$  molecules formed during photolysis combine with XH to produce nitroxide radicals (XO). The amount of nitroxide radicals formed was measured by the electron paramagnetic resonance (EPR) method [19,22]. Furthermore, the formation of nitroxide radicals was not observed when a solution of the complex and XH was kept in the dark or irradiated

in the presence of molecular nitrogen. XH is a specific chemical quencher for  $^1\text{O}_2$  and does not react with superoxide ions ( $\text{O}_2^-$ ), hydrogen peroxide or hydroxyl radicals [22,23].

- (3) Molecular-oxygen-saturated DMF solutions containing  $[\text{Pt}(\text{DHB})(\text{PHEN})]$  ( $5 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ) and different concentrations of XH (ranging from  $1 \times 10^{-1}$  mol  $\text{dm}^{-3}$  to  $1 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) were irradiated at wavelengths in the range 400–800 nm for 1 h. The amount of nitroxide radicals produced after irradiation was measured by the EPR technique.
- (4) Molecular-oxygen-saturated solutions containing  $[\text{Pt}(\text{DHB})(\text{PHEN})]$  ( $5 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ),  $\text{Ni}(\text{DDTC})_2$  ( $5 \times 10^{-6}$  mol  $\text{dm}^{-3}$  or  $1 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ) and different concentrations of XH (from  $1 \times 10^{-1}$  to  $1 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) were irradiated using wavelengths in the range 400–800 nm for 1 h. The amount of nitroxide radicals produced after irradiation was measured by the EPR technique.

The formation of nitroxide free radicals was not observed when solutions of the mononuclear or dinuclear complex and XH were kept in the dark or irradiated in the presence of molecular nitrogen. There was no change in the position or intensity of the absorption bands (between 400 and 800 nm) of the complexes in molecular-oxygen-saturated DMF after irradiation for 2 h. The absorption of the nickel complex in the range 400–800 nm at  $1 \times 10^{-5}$  and  $5 \times 10^{-6}$  mol  $\text{dm}^{-3}$  is less than 0.1% compared with the photosensitizers.

## 3. Results and discussion

### 3.1. Electronic absorption spectra

The electronic absorption spectra of the mononuclear and dinuclear complexes in DMF show five band maxima. The four bands between 200 and 400 nm have been assigned on the basis of the band assignments of mononuclear chloro complexes [24,25]. The fifth band between 450 and 600 nm was observed in all the mononuclear and dinuclear complexes (structures given in Fig. 1) and a representative spectrum of  $[\text{Pd}(\text{DHB})(\text{BPY})]$  (1) is shown in Fig. 2. This fifth absorption band maximum  $\lambda_{\text{max}}$  and its molar extinction coefficient ( $\epsilon_{\text{M}}$ ) are given in Tables 1 and 2. This visible band is strongly dependent on the polarity of the solvent (see Fig. 3). The energy of the band decreases when  $\alpha$ -diimine is changed from BPY to BIQ. The energy of this band is increased relative to  $[\text{M}(\text{DHB})(\text{N-N})]$  and  $[\text{M}(\text{CAT})(\text{N-N})]$  (where CAT is a catecholate anion) [19,26]. From these observations, this band is assigned to the LLCT transition from the highest occupied molecular orbital (HOMO) of DHB to the lowest

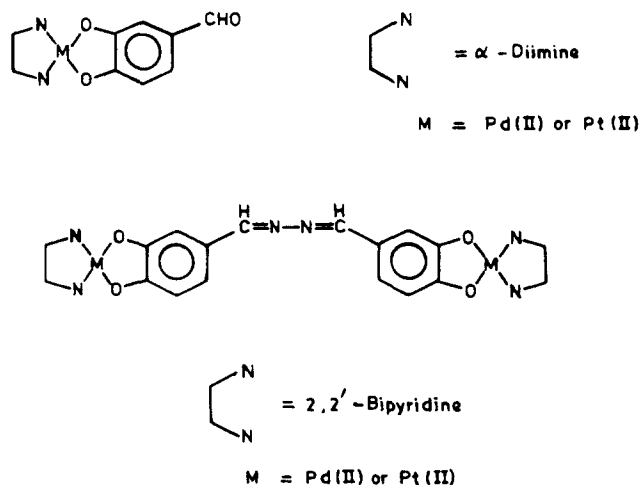


Fig. 1. Structure of: (a)  $[M(DHB)(N-N)]$ ; (b)  $\{[M(BPY)]_2(THB)\}$ .

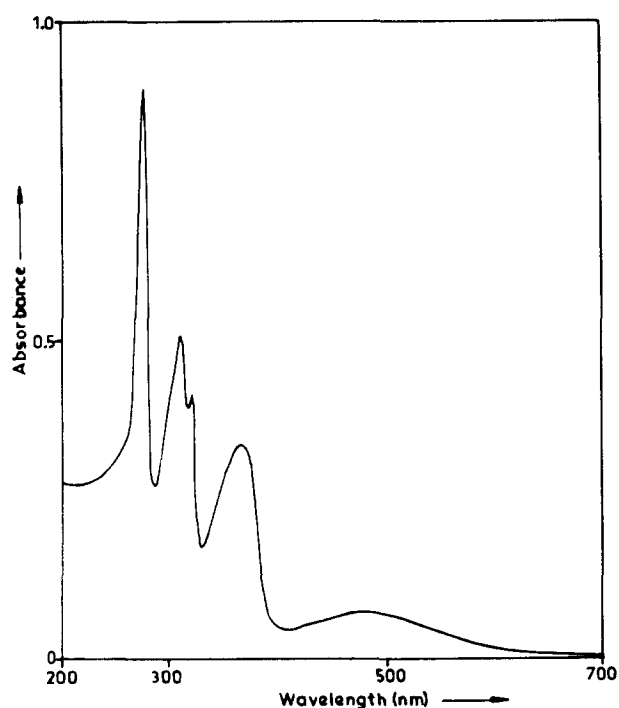


Fig. 2. Electronic absorption spectrum of a  $2 \times 10^{-5}$  mol  $\text{dm}^{-3}$  solution of  $[Pd(DHB)(BPY)]$  in DMF.

unoccupied molecular orbital (LUMO) of the  $\alpha$ -diimine ligand via the metal [8–10,26]. The assignment is also supported by plotting Reichardt's parameters  $E_T$  of the solvents against the absorption maxima  $\nu_{\text{max}}$  in these solvents. A typical plot for  $[Pd(DHB)(BPY)]$  (1) is given in Fig. 3, which shows two separate lines, one for hydroxylic solvents and one for non-hydroxylic solvents [25,27,28].

### 3.2. Determination of the efficiency of photogeneration of $^1O_2$

Molecular-oxygen-saturated DMF solutions of  $[M(DHB)(N-N)]$  ( $200 \mu\text{mol dm}^{-3}$ ) and  $\{[M(BPY)]_2-$

(THB)] ( $100 \mu\text{mol dm}^{-3}$ ) in the presence of XH ( $20 \text{ mmol dm}^{-3}$ ) were irradiated at wavelengths of 400–800 nm for different intervals of time in a merry-go-round apparatus. The  $^1O_2$  molecules formed combine with XH molecules to give 4-hydroxy-2,2,6,6-tetramethyl-4-piperidinyloxy free radicals (XO) which were measured by the EPR method [19,22]. There is a linear relationship between the amounts of free radicals formed and the irradiation time for different mononuclear and dinuclear complexes as shown in Figs. 4–6. Of the mononuclear complexes,  $[Pt(DHB)(PHEN)]$  yields the maximum amount of  $^1O_2$  as it has the highest slope (see Fig. 4), whereas  $[Pd(DHB)(BPY)]$  yields the lowest amount of  $^1O_2$  as it exhibits the smallest slope (see Fig. 5). The relative yields of  $^1O_2$  production referred to  $[Pt(DHB)(PHEN)]$  are given in Table 1.  $\{[Pt(BPY)]_2-(THB)\}$  yields the maximum amount of  $^1O_2$  as it has the highest slope (see Fig. 6), whereas  $[Pd(DHB)(BPY)]$  yields the lowest amount of  $^1O_2$  as it exhibits the smallest slope. The relative yields of  $^1O_2$  production referred to  $\{[Pt(BPY)]_2(THB)\}$  are given in Table 2. The values of the relative efficiency were calculated after correcting for the amount of light absorbed using the relative integrated areas under the absorption curves; these are also given in Tables 1 and 2. The relative efficiencies of the mononuclear complexes follow the order:  $[Pt(DHB)(PHEN)] > [Pt(DHB)(DPP)] > [Pt(DHB)(BIQ)] > [Pt(DHB)(BPY)] > [Pd(DHB)(DPP)] \geq [Pd(DHB)(PHEN)] > [Pd(DHB)(BIQ)] \geq [Pd(DHB)(BPY)]$ . The relative efficiencies of the dinuclear complexes, compared with the corresponding mononuclear complexes, follow the order:  $\{[Pt(BPY)]_2(THB)\} > [Pt(DHB)(BPY)] > \{[Pd(BPY)]_2(THB)\} > [Pd(DHB)(BPY)]$ .

The above results suggest that the photo-oxidation of XH sensitized by mononuclear and dinuclear com-

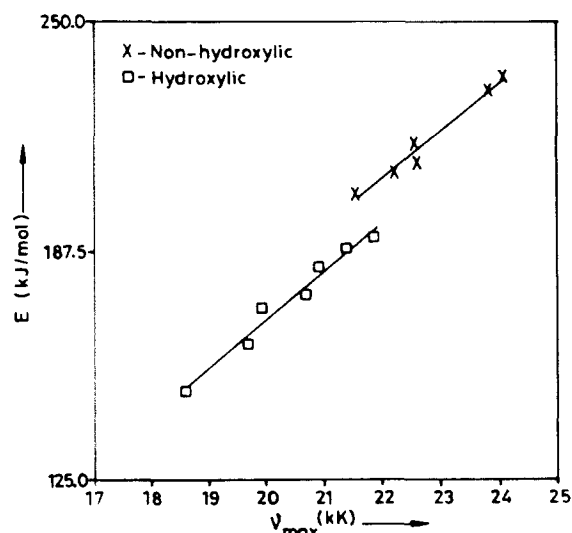


Fig. 3. Plots of  $E_T$  ( $\text{kJ mol}^{-1}$ ) vs.  $\nu_{\text{max}}$  ( $\text{kK}$ ,  $1 \text{ kK} = 10^3 \text{ cm}^{-1}$ ) for LLCT in various solvents.

Table 1

Electronic absorption, relative yield and efficiency of mononuclear Pt(II) and Pd(II) complexes for the photosensitized generation of  $^1\text{O}_2$ 

Complex	$\lambda_{\text{max}}$ (nm)	$\epsilon$ ( $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )	Relative yield of $^1\text{O}_2$ production (referred to [Pt(DHB)(PHEN)])	Relative efficiency <sup>a,b</sup> of $^1\text{O}_2$ production (referred to [Pt(DHB)(PHEN)])
[Pt(DHB)(PHEN)]	475	1650	1.00	1.00
[Pt(DHB)(DPP)]	518	8970	0.23	0.56
[Pt(DHB)(BIQ)]	621	22860	0.20	0.49
[Pt(DHB)(PBY)]	496	8220	0.30	0.19
[Pd(DHB)(PHEN)]	476	3070	0.10	0.11
[Pd(DHB)(DPP)]	492	4070	0.12	0.13
[Pd(DHB)(BIQ)]	598	2420	0.01	0.01
[Pd(DHB)(BPY)]	478	3730	0.01	0.01

<sup>a</sup> Relative integrated areas under the absorption curves between 400 and 800 nm of [Pt(DHB)(PHEN)], [Pt(DHB)(DPP)], [Pt(DHB)(BIQ)], [Pt(DHB)(BPY)], [Pd(DHB)(PHEN)], [Pd(DHB)(DPP)], [Pd(DHB)(BIQ)] and [Pd(DHB)(BPY)] for  $2 \times 10^{-4} \text{ mol dm}^{-3}$  solutions are 1.00, 0.41, 0.41, 1.60, 0.99, 0.91, 0.88 and 0.94 respectively.

<sup>b</sup> Efficiency of  $^1\text{O}_2$  generation is about 11% of that of rose bengal.

Table 2

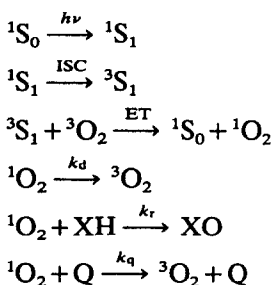
Electronic absorption, relative yield and efficiency of dinuclear Pt(II) and Pd(II) complexes and their corresponding mononuclear complexes for the photosensitized generation of  $^1\text{O}_2$ 

Complex	$\lambda_{\text{max}}$ (nm)	$\epsilon$ ( $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )	Relative yield of $^1\text{O}_2$ production (referred to [Pt(BPY)] <sub>2</sub> (THB))	Relative efficiency <sup>a,b</sup> of $^1\text{O}_2$ production (referred to [Pt(BPY)] <sub>2</sub> (THB))
[Pt(BPY)] <sub>2</sub> (THB)	510	5660	1.00	1.00
[Pt(DHB)(BPY)]	496	8220	0.50	0.24
[Pd(BPY)] <sub>2</sub> (THB)	465	7040	0.08	0.17
[Pd(DHB)(BPY)]	478	3730	0.05	0.04

<sup>a</sup> Relative integrated areas under the absorption curves between 400 and 800 nm of [Pt(BPY)]<sub>2</sub>(THB), [Pt(DHB)(BPY)], [Pd(BPY)]<sub>2</sub>(THB) and [Pd(DHB)(BPY)] for  $2 \times 10^{-4} \text{ mol dm}^{-3}$  (mononuclear) and  $1 \times 10^{-4} \text{ mol dm}^{-3}$  (dinuclear) solutions are 1.00, 2.04, 0.46 and 1.10 respectively.

<sup>b</sup> Efficiency of  $^1\text{O}_2$  generation is about 8.5% of that of rose bengal.

plexes involves  $^1\text{O}_2$  as an intermediate; the triplet state of the LLCT transition in mononuclear and dinuclear complexes is responsible for the production of  $^1\text{O}_2$  by energy transfer [13]. Thus the following mechanism is suggested for the reaction



where  $^1\text{S}_0$  is the ground state of the sensitizer (mononuclear or dinuclear complex),  $^1\text{S}_1$  and  $^3\text{S}_1$  are its first excited singlet and triplet states respectively,  $h\nu$  is the energy of a photon, ISC denotes intersystem crossing, ET denotes energy transfer,  $k_d$  is the rate constant of quenching of  $^1\text{O}_2$  by a DMF molecule,  $k_r$  is the rate constant of chemical quenching of  $^1\text{O}_2$  by XH to produce

XO and  $k_q$  is the rate constant of physical quenching of  $^1\text{O}_2$  by Ni(DDTC)<sub>2</sub> (Q). On the basis of the assumption of the above mechanism, the rate of formation of XO free radicals by the oxidation of XH with  $^1\text{O}_2$ , using the steady state approximation, can be given by

$$d[\text{XO}]/dt = I_{\text{abs}} \phi_{1\text{O}_2} (k_r[\text{XH}]/k_t[\text{XH}] + k_d) \quad (1)$$

where  $I_{\text{abs}}$  is the intensity of irradiation and  $\phi_{1\text{O}_2}$  is the quantum yield of  $^1\text{O}_2$  production. If  $k_r$ , [XH] and  $k_d$  are kept constant, the slope of the plot of the amount of nitroxide radical formed vs. the time of irradiation will be directly proportional to  $I_{\text{abs}} \phi_{1\text{O}_2}$  for the above solutions. By correcting for the relative amounts of light absorbed or the relative integrated areas under the absorption curves for the different complexes, the relative quantum yields can be obtained using the following equation

$$(\phi_{1\text{O}_2})_2 / (\phi_{1\text{O}_2})_1 = (\text{slope})_2 \times (I_{\text{abs}})_1 / (\text{slope})_1 \times (I_{\text{abs}})_2 \quad (2)$$

The efficiency of the complexes for the photogeneration of  $^1\text{O}_2$  depends on several factors, such as the substituent present in the  $\alpha$ -diimine and the non-

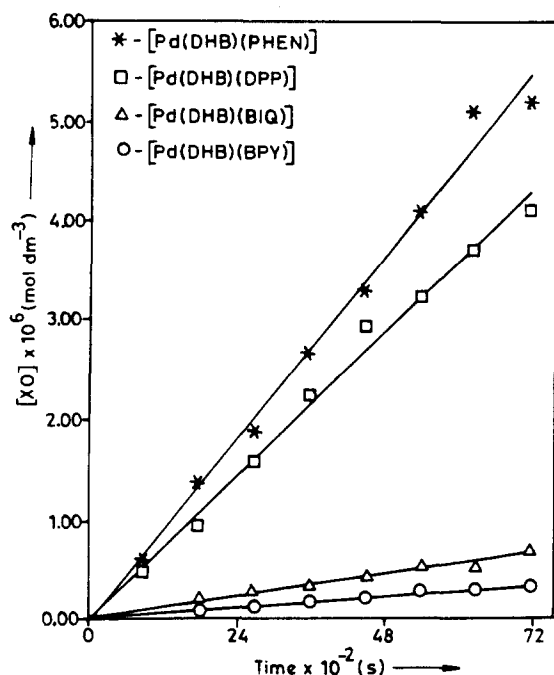


Fig. 4. Plots of XO free radical concentration vs. irradiation time for solutions of  $[\text{Pd}(\text{DHB})(\text{N-N})]$  ( $2 \times 10^{-4} \text{ mol dm}^{-3}$ ) in the presence of  $\text{XH}$  ( $2 \times 10^{-2} \text{ mol dm}^{-3}$ ) in DMF.

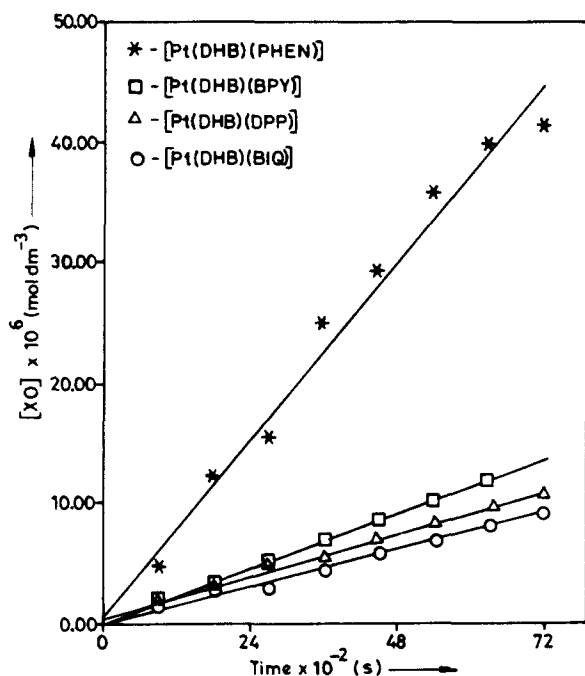


Fig. 5. Plots of XO free radical concentration vs. irradiation time for solutions of  $[\text{Pt}(\text{DHB})(\text{N-N})]$  ( $2 \times 10^{-4} \text{ mol dm}^{-3}$ ) in the presence of  $\text{XH}$  ( $2 \times 10^{-2} \text{ mol dm}^{-3}$ ) in DMF.

polarity of the  $\alpha$ -diimine ligand in the metal complex.

In the dinuclear complexes, the photosensitizing efficiency of  $^1\text{O}_2$  production is about 400% greater than that of the corresponding mononuclear complexes (see Table 1). Recently, a dinuclear complex containing one Ru(II) ion and one Pd(II) ion has been shown to be 150% more efficient in producing  $^1\text{O}_2$  than the cor-

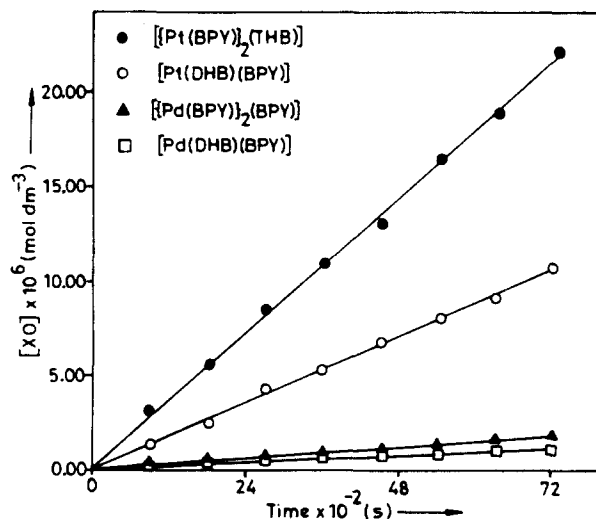


Fig. 6. Plots of XO free radical concentration vs. irradiation time for solutions of  $[\text{M}(\text{DHB})(\text{BPY})]$  ( $2 \times 10^{-4} \text{ mol dm}^{-3}$ ) and  $\{[\text{M}(\text{BPY})]_2(\text{THB})\}$  ( $1 \times 10^{-4} \text{ mol dm}^{-3}$ ) in the presence of  $\text{XH}$  ( $2 \times 10^{-2} \text{ mol dm}^{-3}$ ) in DMF.

responding mononuclear complex  $[\text{Pd}(\text{CAT})(\text{BPY})]$  [12,29].

The data given in Table 1 suggest that the Pt(II) complexes are better sensitizers than the corresponding Pd(II) complexes. This observation can be rationalized on the basis of the following arguments. On moving from Pd(II) to Pt(II), the crystal field splitting energy increases usually by 30%–50% [30]. It is assumed that each chromophore in the mononuclear and dinuclear complexes has  $C_{2v}$  symmetry and the  $^3\text{A}_2$  (or  $^1\text{A}_2$ ) state is expected to have much higher energy than the  $^3(\text{d},\pi^*)$  state in the Pt(II) complexes than the Pd(II) complexes [31,32]. Thus the  $^3\text{A}_2$  ( $^1\text{A}_2$ ) state of Pt(II) is less available for radiationless decay than that of Pd(II). Hence the Pt(II) complexes are better photosensitizers than the corresponding Pd(II) complexes. A similar trend has also been observed for the  $\alpha$ -diimine complexes of Pt(II) and Pd(II) with 3,4-dihydroxybenzoic acid anion [13].

### 3.3. Determination of $k_q$

The quenching of the photo-oxidation of XH sensitized by complexes 1–10 was studied using  $\text{Ni}(\text{DDTC})_2$  as a physical quencher of  $^1\text{O}_2$  [17]. In these experiments, molecular-oxygen-saturated solutions containing 6 ( $5 \times 10^{-5} \text{ mol dm}^{-3}$ ),  $\text{Ni}(\text{DDTC})_2$  ( $1 \times 10^{-5}$  or  $5 \times 10^{-5} \text{ mol dm}^{-3}$ ) and different concentrations of XH (varying from  $1 \times 10^{-2}$  to  $1 \times 10^{-3} \text{ mol dm}^{-3}$ ) were irradiated for 1 h with mixing at regular intervals.

In the presence of quencher (Q), we have

$$1/[\text{XO}] = 1/[^1\text{O}_2] \{1 + (k_d + k_q[\text{Q}])/k_r[\text{XH}]\} \quad (3)$$

From a plot of  $1/[\text{XO}]$  against  $1/[\text{XH}]$ , we have

$$k_q = (\text{slope} \times k_r / \text{intercept} \times [Q]) - k_d / [Q] \quad (4)$$

A plot of  $1/[XO]$  against  $1/[XH]$  gives two straight lines with the same intercept but with different slopes for two different concentrations of Q, as shown in Figs. 7 and 8 for dinuclear and mononuclear complexes respectively. By substituting the values of  $k_d = 1.43 \times 10^5 \text{ s}^{-1}$  [33],  $k_r = 2.45 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  [22,34,35], the slope and the intercept ( $\text{slope} = 1/[^1O_2](k_q[Q] + k_d/k_r)$  and  $\text{intercept} = 1/[^1O_2]$ ),  $k_q$  can be calculated for the dinuclear and mononuclear complexes. The values of

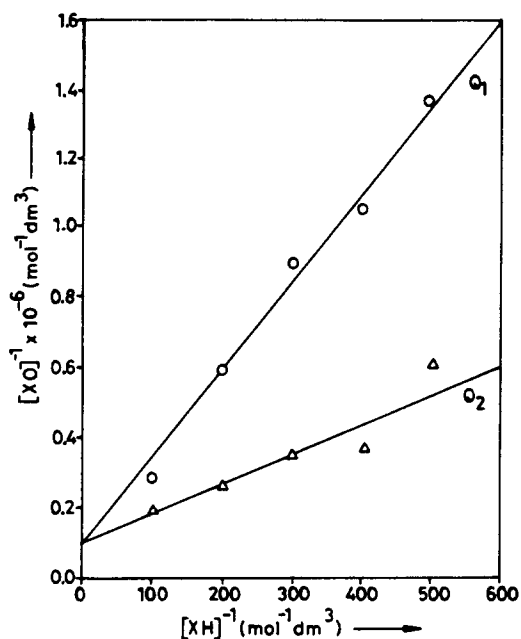


Fig. 7. Plots of the reciprocal XO free radical concentration vs. the reciprocal XH concentration in the presence of  $Ni(DDTC)_2$  ( $Q_1 = 1 \times 10^{-5}$  and  $Q_2 = 1 \times 10^{-6} \text{ mol dm}^{-3}$ ) using  $\{Pt(BPX)_2(THB)\}$  ( $2 \times 10^{-5} \text{ mol dm}^{-3}$ ) as photosensitizer in DMF.

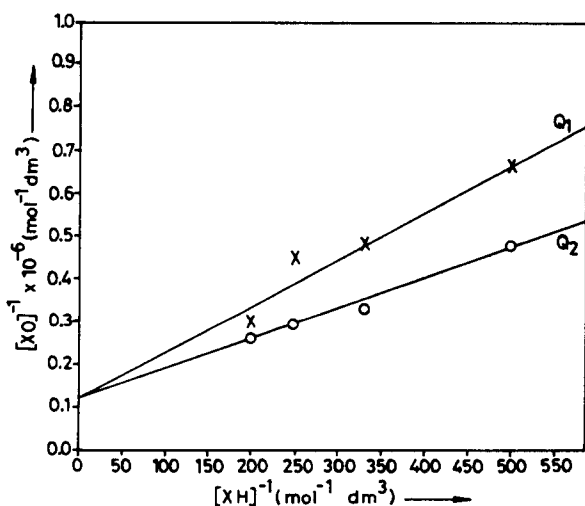


Fig. 8. Plots of the reciprocal XO free radical concentration vs. the reciprocal XH concentration in the presence of  $Ni(DDTC)_2$  ( $Q_1 = 1 \times 10^{-5}$  and  $Q_2 = 5 \times 10^{-6} \text{ mol dm}^{-3}$ ) using  $\{Pt(DHB)(PHEN)\}$  ( $5 \times 10^{-5} \text{ mol dm}^{-3}$ ) as photosensitizer in DMF.

$k_q$  for  $\{Pt(BPY)_2(THB)\}$  are  $4.8 \times 10^{10}$  and  $6.3 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  for  $1 \times 10^{-5} \text{ mol dm}^{-3}$  and  $1 \times 10^{-6} \text{ mol dm}^{-3}$  of the quencher respectively. In addition, the  $k_q$  values for  $\{Pt(DHB)(PHEN)\}$  are  $0.6 \times 10^{10}$  and  $1.1 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  for  $1 \times 10^{-5} \text{ mol dm}^{-3}$  and  $5 \times 10^{-6} \text{ mol dm}^{-3}$  of the quencher respectively. The average  $k_q$  values are close to those of a diffusion-controlled reaction, which is consistent with quenching by the energy transfer mechanism. The slopes of the linear plots in Figs. 7 and 8 increase with increasing concentrations of the quencher without a change in the intercept of the plots. Thus only physical quenching of  $^1O_2$  by the nickel complex is involved and there is no direct involvement of the excited states of the photosensitizers with the nickel complex [33].

#### 4. Conclusions

This study shows that several mixed-ligand palladium(II) and platinum(II) complexes exhibiting a LLCT band in the visible region can photosensitize the generation of  $^1O_2$ . The extent of  $^1O_2$  generation photosensitized by the above complexes depends on the nature of the metal ion, the number of metal ions, the nature of the  $\alpha$ -diimine ligand and the extent of distortion from a square planar geometry of the complex.

#### Acknowledgement

T.S.S. thanks the Department of Science and Technology (Government of India), New Delhi for financial support of this research.

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